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Direct time-resolved studies of photochemical reactions in liquids by X-ray scattering

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Abstract

The structural characterization of photochemical transients in solution by time-resolved X-ray diffraction is discussed. The photodissociation reaction of HgI_2 is studied as model system in order to explore the possibilities and limitations of state-of-the-art synchrotron sources. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The knowledge of the structure of intermediates is essential for the understanding of a chemical reaction. Femtosecond spectroscopy has provided during the last decade unprecedented insight regarding the existence and evolution of these intermediates, which were characterized via their electronic and vibrational spectra [1]. The corresponding structural information is mainly obtained by calculations. While the relation between spectral response and structural change becomes more reliable and precise with the development of quantum chemical calculations, it is still desirable to access directly the structural information. Indeed, at early times, when the system is not very far from stable configurations,

optical spectroscopy data are readily linked to structural changes. However, as the distance between reactants increases, this relation becomes less reliable and optical spectroscopy less informative. X-ray diffraction is a method of choice to access structural information directly. On the one side as a control of the calculated structures, and more important, in situations when the spectral changes are very small for relatively large structural changes. This is, for example, the case of dissociation reactions, when, at larger distances of the fragments, the spectra change only very little or for the solvent structure around reaction intermediates. Direct, time-resolved structural studies must therefore be developed. At present, a great effort is underway to develop time-resolved X-ray diffraction methods [2]. Different options include the use of femtosecond, laser-generated pulsed X-ray sources, which are naturally synchronized with a laser pulse that initiates the reaction, the use of the existing most advanced

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synchrotron sources with ca. 100 ps pulses and the extension of this sources to even higher time resolution, as well as the time resolution of the diffracted signal via different schemes.

Time-resolved structural changes, following laser excitation, have recently been measured in a number of crystals. In particular, the photodissociation of CO in myoglobin and excited state geometry changes were successfully studied by these methods [3,4]. However, only few reactions of general interest can be studied in the crystalline phase, and most systems will have to be studied in the gas or liquid phase. Solutions are much simpler regarding sample requirements. Structural information in solutions is also obtained by X-ray scattering. This technique is simple to use but less informative than crystal diffraction and more demanding regarding the X-ray flux and the detection.

It is the objective of this work to explore the possibilities of time-resolved X-ray diffraction for the study of structural changes during such reactions and to present results on the photodissociation reaction of HgI_2 in methanol solution. This simple reaction is reversible and has already been studied in detail by purely optical spectroscopic techniques as well as molecular dynamics calculations [5]. Our study has been able to clearly identify changes in the X-ray diffraction signal associated with the laser photolysis. Most important is that our study shows the possibilities and limitations of the most advanced present day synchrotron sources and also indicates ways to overcome these limitations in future studies. In Section 2, we shortly summarize what is known about the photodissociation reaction of $\text{HgI}_2 \rightarrow \text{HgI} + \text{I}$. The experiment is described in Section 3, and in Section 4 we discuss the data reduction. Finally in Section 5, we show the results obtained and conclude by indicating the future developments.

2. HgI_2 photodissociation

Geometry: X-ray diffraction studies indicate that I–Hg–I in DMSO and DMF solution is bent since

the I–I distance is slightly shorter than twice the Hg–I distance. Two studies give values for these distances of $2.599 \pm 0.005 \text{ \AA}$ / $5.13 \pm 0.04 \text{ \AA}$ and 2.625 \AA / 5.12 \AA , corresponding to an angle of 161° and 155° , respectively [6,7]. Spectroscopic studies of chemiluminescent HgI indicate Hg–I distances of 2.8 and 3.3 \AA in the ground and the first excited state, respectively [8,9].

Photodissociation: HgI_2 in methanol solution has its first absorption maximum at 270 nm. Excitation in this band leads to dissociation into HgI and atomic iodine as well as complete dissociation. Optical spectroscopic studies with femtosecond time resolution of the dissociation reaction $\text{HgI}_2 \rightarrow \text{HgI} + \text{I}$ in different solvents have been done [10–12]. Vibrationally excited HgI is created and relaxes within 3 ps, a result reproduced by molecular dynamics simulations [13]. The HgI absorption decays in part due to geminate recombination and on a microsecond time scale due to diffusion limited recombination. Anisotropy measurements of the HgI_2 photodissociation in ethanol yield a biphasic decay with a sub-picosecond component attributed to the decay of the rotational coherence of inertial motion at the bath temperature, interrupted at later times by solvent collisions.

The distribution of the excess energy between rotational and translational energy of the fragments depends on the geometry of HgI_2 . This initial geometry as well as the relaxation dynamics following photodissociation is solvent dependent. Direct structural studies of this system at the earliest times are not accessible by present day technology. However, the diffusional motion at times greater than a few picoseconds can be studied. The initial, fairly sharp distribution of fragments is washed out at later times by diffusion. In this study, only this distribution at later times is probed, and the expected scattering signal after photolysis is that of a random distribution of HgI_2 as well as the equilibrated fragments of HgI, Hg, and I. In this study, the solvent reorganization around the products formed corresponds to equilibrium structures, but its measurement requires a very high precision, since the expected changes in the scattering signal are very small.

3. The experiment

The experiment has been done at the European Synchrotron Radiation Facility (ESRF), one of the three large third generation synchrotrons in the world. Beamline ID9 is equipped with a femtosecond laser system, the repetition frequency of which is slaved to the synchrotron bunch clock, and with a phase locked chopper selecting 150 ps X-ray pulses at 900 Hz (the laser amplifier repetition frequency) from the ESRF single-bunch mode [14]. Under these conditions, the X-ray flux is 3–4 orders of magnitude lower than for static measurements without chopper. The X-ray energy was 16.45 KeV ($\lambda = 0.75317 \text{ \AA}$).

The laser system: The femtosecond laser system consists of a Ti:Sa mode-locked oscillator producing 100 fs pulses at 800 nm. The laser frequency of 88.05 MHz corresponds to the fourth sub-harmonic of the synchrotron bunch clock. These pulses seed a Ti:Sa chirped pulse amplifier pumped at 900 Hz by a Nd:YLF laser. The resulting 100 fs pulses of about 0.5 mJ are frequency doubled and tripled with BBO crystals. The energy of the final 267 nm pulses at the sample is 6 μJ . The overall jitter between these laser pulses and the synchrotron X-ray pulses is 5 ps (rms).

The sample: The sample is a 35 mM methanol solution of HgI_2 (Sigma-Aldrich 99.999%, used as received). This concentration corresponds to an average nearest neighbor distance between solute molecules of 2 nm. The molar extinction of HgI_2 in methanol at the excitation wavelength of 267 nm is $5900 \text{ dm}^3/\text{mol}/\text{cm}$, which means that 90% of the incident photons are absorbed within $50 \mu\text{m}$. However, because of possible aggregation at these high concentrations and non-linear excitation conditions, the Lambert–Beer law may no longer apply.

This solution was pumped through a free jet. The use of a free jet is required, because the intensity of the focussed pump laser pulses is close to the breakdown of the sample and would lead to the destruction of any enclosure. In addition, scattering from windows is eliminated. The jet was running with a velocity of about 5 m/s,

driven by a peristaltic pump. A glass capillary served as nozzle for the circular jet of $360 \mu\text{m}$ diameter. Any contact between the solution and metallic parts, leading to decomposition of HgI_2 , was avoided this way. Care was taken to minimize the irregular flow induced by the pump in using two branches with phase shifted rollers in the pump and by damping the residual fluctuations in a reservoir and via the use of soft tubing.

HgI_2 in methanol is a toxic solution. For safety reasons, the vertical jet had therefore to be installed in a sample cell with two Kapton windows of $13 \mu\text{m}$ thickness for the X-ray transmission and a perpendicular entrance channel for the laser beam.

The geometry: Fig. 1 shows the geometry of the overlap of the jet and the laser and X-ray beams. Both the X-ray and laser beams are in the horizontal plane intersecting the vertical jet at right angles. The diameter of the laser beam is $120 \mu\text{m}$ and the cross section of the X-ray beam is limited to $100 \mu\text{m} \times 220 \mu\text{m}$, reducing the available X-ray flux by a factor of 2. No further limitation of the X-ray beam was made in order to be less sensitive to small drifts in the geometry of the jet and the laser and X-ray beams.

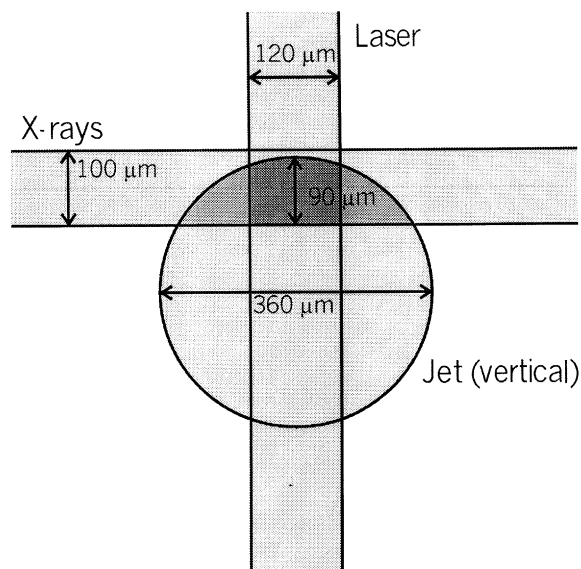


Fig. 1. Geometry of the experiment.

Data acquisition: The scattering signal was recorded at a time delay of 500 ps after the laser excitation. This signal was acquired with a MAR CCD area detector for time intervals of 10 min toggling the laser between successive measurements. Over these time intervals and under the condition of the experiment, the dark current of the detector was about 0.5% of the total signal. Since the difference between the signals recorded with the laser on and off is estimated to amount to about 10^{-3} of the total scattering signal, and because this total signal is not sufficiently strong to be recorded with the required precision, laser-on/laser-off difference signals have to be averaged. Given the resulting time scale of the experiment, any small drift and instability of the experiment may mask the photo-induced signal. The data reduction and analysis becomes therefore a crucial issue and is presented in more detail below.

4. Data reduction and analysis

The first step of data reduction is annular integration of the diffraction image, applying geometry correction for intensities, polarization and detector tilt. The resulting curve will be called ‘diffraction pattern’, and represents the dependence of the diffracted intensity on the angle 2θ between incident and diffracted beams. Fig. 2 shows a typical diffraction pattern obtained without laser excitation, which, on this scale, would be indistinguishable from the one obtained with laser excitation.

In order to extract the effect of laser excitation on the diffraction pattern, all parameters that drift during data acquisition must be considered: the X-ray flux, which is not simply related to the storage ring current and whose decrease in time leads to drifts because of the changing heat load suffered by the beam-line components, other geometry instabilities, sample composition, temperature drifts and detector drift and noise. Even when alternating laser-on and laser-off data acquisitions, normalization is absolutely required. In addition, the dark signal of the CCD camera is

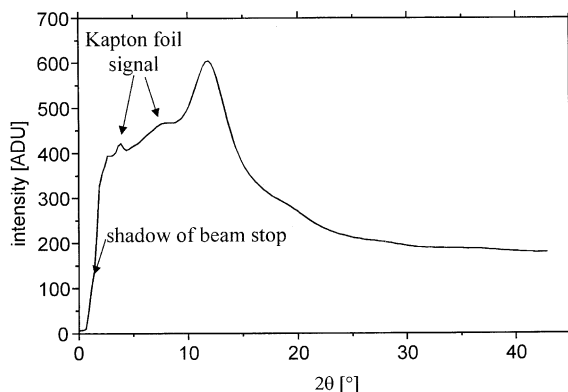


Fig. 2. Static diffraction pattern of a 35 mM solution of HgI_2 in methanol.

unstable, an instability not restricted to an overall amplitude change.

The following procedure was used for treating the diffraction pattern: (i) In order to compensate for signal drifts, the difference is calculated between each laser-on diffraction pattern and an *optimized* linear combination of the two closest laser-off diffraction patterns, once taken into account the dark signal of the CCD camera; (ii) This dark signal not being stable, a dark pattern with an amplitude *optimized* for each of the above mentioned differences was used. The criteria for these optimizations are the following: (a) Since for large values of 2θ the diffraction signal approaches zero, this condition is also imposed for the difference; (b) The peak (due to methanol) observed at $2\theta = 12^\circ$ in the diffraction pattern of Fig. 2 should be suppressed in the difference pattern by the normalization.

5. Results

Given the precision of our measurements, only the contribution of HgI_2 and its fragments to the diffracted signal was evaluated. At the dilution of HgI_2 , the Debye equation for gas diffraction can be used. The coherent part of the diffracted intensity (in electron units) is

$$I_{\text{eu}} = \sum_m \sum_n f_m f_n \frac{\sin(kr_{mn})}{kr_{mn}} \quad (1)$$

with f_m being the form factor for atom m , $k = (4\pi \sin\theta)/\lambda$, with θ being the half angle between incident and diffracted beams, and λ the X-ray wavelength. We disregard here the inelastic Compton scattering, which carries no structural information and therefore cancels out in the difference between *laser-on* and *laser-off*. From static measurements, we know that diffraction due to HgI_2 contributes about 8% to the total observed signal (including solvent, air, and windows). The photolysis in the scanned area is expected to be 10%. Using Eq. (1) with the known atomic distances of HgI_2 (2.6 Å) [6,7] and of the photolysis fragment HgI (2.8 Å) [15] and neglecting all recombination processes, the difference signal for our sample due to photolysis is expected to be of the order of 0.1% of the total scattering signal.

Fig. 3 shows the observed difference signal as compared to calculated signals for partial ($\text{HgI} + \text{I}$) and total dissociation of HgI_2 . In Fig. 3, the calculated signals have been divided by factors of 4 and 7 for partial and total dissociation, respectively. Part of this difference is due to the neglect of recombination processes. Regarding the shape of the difference curve, the expected decrease at small angles is clearly observed. Even though the statistics is rather poor, the deviations of experiment from theory may indicate more complex processes: the presence of higher aggregates of HgI_2 , formation of I_2 , solvent reorganization around

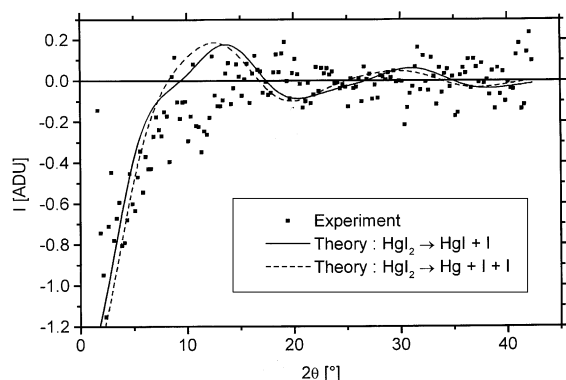


Fig. 3. Observed difference signal, obtained by averaging 18 difference patterns, compared with signals calculated for partial and complete photodissociation of HgI_2 .

products, solvent ionization, etc. At this stage, however, a quantitative analysis of these factors is not warranted and would be too speculative.

The most important improvement of the experiment is the increase of the X-ray flux. A gain in flux of 25–50 can be obtained by using an in-vacuum undulator. In addition, the X-ray bandwidth can be adjusted for liquid scattering experiments, which do not require a resolution $E/\Delta E$ of more than 10^2 as compared to 10^4 at present. This can be achieved using multilayers instead of monochromator crystals or using the fundamental frequency of the undulator directly. The X-ray flux may therefore be increased by a factor of more than 1000, improving not only the signal-to-noise ratio, but reducing also the importance of drifts, due to the shortened measurement times. In addition, gas detectors with an annular mask, enabling the use of lock-in techniques, are projected, so that the tedious and uncertain normalization procedures are largely avoided.

In view of these developments, which are under way at the ESRF, the perspective of liquid diffraction experiments is therefore rather promising, given the results obtained in this exploratory study. Regarding the HgI_2 system, many of the unresolved questions of the present work can be addressed and resolved. Even more important is that the implantation of such experiments in future synchrotron sources with significantly reduced pulse duration is fully warranted, since the increased time resolution is essential for the most important issues of structural changes at early times.

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References

- [1] A.H. Zewail, *Angew. Chem. (Int. Ed.)* 39 (2000) 2587.
- [2] *Proceedings of the SPIE*, Vol. 3451, 1998, pp. 1–189.

- [3] V. Srajer, Tsu-yi-Teng, T. Ursby, C. Pradervand, Zhong-Ren, S.I. Adachi, W. Schildkamp, D. Bourgeois, M. Wulff, K. Moffat, *Science* 274 (1996) 1726.
- [4] S. Techert, F. Schotte, M. Wulff, *Phys. Rev. Lett.* 86 (2001) 2030.
- [5] N. Pugliano, A.Z. Szarka, R.M. Hochstrasser, *J. Chem. Phys.* 104 (1995) 5062.
- [6] F. Gaizer, G. Johansson, *Acta Chem. Scand.* 9 (1968) 3013.
- [7] M. Sandström, *Acta Chem. Scand.* 32 (1978) 627.
- [8] F.M. Zhang, D. Oba, D.W. Setser, *J. Phys. Chem.* 91 (1987) 1099.
- [9] K.S. Viswanathan, J. Tellinghuisen, *J. Molec. Spectrosc.* 98 (1983) 185.
- [10] N. Pugliano, D.K. Palit, A.Z. Szarka, R.M. Hochstrasser, *J. Chem. Phys.* 99 (1993) 7273.
- [11] N. Pugliano, A.Z. Szarka, S. Gnanakaran, M. Triefel, R. Hochstrasser, *J. Chem. Phys.* 103 (1995) 6498.
- [12] N. Pugliano, A.Z. Szarka, R. Hochstrasser, *J. Chem. Phys.* 104 (1996) 5062.
- [13] S. Ganakaran, R.M. Hochstrasser, *J. Chem. Phys.* 105 (1996) 3486.
- [14] M. Wulff, F. Schotte, G. Naylor, D. Bourgeois, K. Moffat, G. Mourou, *Nucl. Instrum. and Meth. A* 398 (1997) 69.
- [15] K.S. Viswanathan, A. Ron, O. Schnepp, *J. Chem. Phys.* 50 (1969) 2502.